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Cathode systems for the electrolytic production of aluminum

Field of the Invention

- 5 The invention relates to cathode systems for the electrolytic production of aluminum, in particular ones having an improved operating life.

Background of the Invention

- 10 In the electrolytic production of metallic aluminum in the Hall-Héroult process, aluminum oxide dissolved in about 20 times its amount of molten cryolite ($\text{Na}_3[\text{AlF}_6]$) as flux is decomposed by means of direct current (at a voltage of from 4 to 5 V and a current of from 80 000 to
15 500 000 A) at a temperature of about 960 °C in electrolysis cells. The liquid aluminum collects on the bottom of the carbon-lined tank serving as cathode under the melt which largely protects it from reoxidation. The carbon electrodes acting as anode (block or Söderberg
20 anodes) are gradually consumed by the oxygen which is liberated.

- Suitable electrolysis cells usually comprise a steel tank which is lined on the inside with a thermally insulating
25 material. The bottom of the electrolysis cells comprises a plurality of cathode blocks which are arranged in parallel on the insulating material and whose joins between one another and to the outer wall are sealed by means of ramming paste paste comprising mixtures of
30 carbon granules and black coal tar or black coal tar pitch. The material for the cathode blocks usually comprises anthracite (now also graphite or coke or

mixtures thereof with anthracite) which is calcined at 1 200 °C or above, then milled and classified according to particle size. A suitable particle size fraction is mixed with pitch and shaped to produce blocks. The pitch
5 binder is subsequently converted at elevated temperature into a material consisting essentially of carbon. A distinction is made here between graphitized (treatment at about 3 000 °C), "semigraphitized" (treatment at about 2 300 °C), "semigraphitic" (graphitic particles, but
10 treatment of the block at about 1 200 °C) and amorphous blocks (particles are not graphitized or only partially graphitized, treatment of the block at about 1 200 °C).

The electric current is conducted away from the liquid
15 electrolyte and the aluminum melt covering the bottom by means of steel bars or collectors which are connected electrically to the cathode blocks.

Consumption of the material of the cathode blocks, too,
20 as a result of erosion is observed, and this determines the life of the electrolysis cell, which is usually from 1 500 to 3 000 days. This erosion is not distributed uniformly over the length of the cathode blocks, but instead, especially in the case of graphitized cathode
25 blocks, two maxima in the removal of material are observed in the vicinity of the side blocks and a minimum is observed in the middle of the length of the cathode blocks (W-shaped profile). Due to the nonuniform removal of material, the useful life is naturally determined by
30 the areas having the greatest removal of material.

The useful life of the cathode blocks has been the subject of numerous studies.

In J. Appl. Electrochemistry **19** (1989), pp. 580 to 588, M. Sørli and H.A. Øye have reported a systematic study on the various influences on the cathode materials, seals and side blocks and their effects on the useful life.

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In EP-A 0 284 298, improved sealing materials are described for joining the cathode blocks. They have less tendency to suffer from crack formation than known sealing materials and thus reduce the risk of failure.

10 However, this measure does not alter the nonuniform corrosion over the length of the cathode blocks.

An improvement in the flow of electricity between the steel collectors (in this case configured as plates) and the cathode by use of contact pins in the interface is described in WO-A 97/48838 and in Aluminium 72, 1996, number 11, pages 822 to 826. However, the installation of these contact pins and the machining of the recesses on the adjoining part incur considerable expense.

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In WO-A 00/46426 a one-piece graphite cathode block is described which has varying specific electrical resistances in a direction parallel to the longitudinal axis, with the resistance near the ends of the block being higher than in the middle. These differences are achieved by different heat treatment in graphitization, namely the use of temperatures of from 2 200 to 2 500 °C in the region of the ends and from 2 700 to 3 000 °C in the region of the middle of the cathode blocks. Such different temperatures can be achieved by lack of insulation of the graphitising furnaces. Another possibility is to choose appropriately different current densities during graphitization, and thus distribute the Joule heat nonuniformly over the cathode block to be

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graphitized. While the first possibility is to be rejected for economic reasons, the second possibility results in additional complication of the graphitization step which has to be optimized in each case to the specific cathode shape.

Another embodiment of a cathode having an improved life is described in WO-A 00/46427. Here, a graphite cathode is impregnated with a carbonizable substance under reduced pressure at elevated temperature, with temperature and time having to be selected so that the substance is sufficiently fluid to fill the pores of the cathode, and the impregnated cathode is subsequently carbonized at a temperature below 1 600 °C. This requires additional working steps in manufacture of the cathode.

Finally, in WO-A 00/46428, a graphite cathode is described whose specific electrical resistance is higher in the direction perpendicular to its longitudinal axis than in the direction of the longitudinal axis. This difference in resistance is achieved by use of different materials for producing the cathode, with at least some being anisotropic, and by production under conditions which promote orientation of particles, e.g. extrusion or vibromoulding. This procedure requires specific (additional) materials and adapted production processes.

All the measures mentioned thus imply particularly increased costs in the production of the cathodes.

Summary of the invention

It is therefore an object of the invention to make the removal of material from the cathode blocks as uniform as possible over the length of the blocks by means of simple

measures. In particular, it is desirable to leave the production process for the cathodes uniform so that the variety of production measures is not increased unnecessarily.

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This object is achieved by dividing the conduction of electric currents from the carbon cathode into a plurality of zones. This can be achieved by dividing the contact composition or ramming paste providing the electrical connection between the cathode and the collectors into a plurality of zones in which materials having differing conductivity or differing electrical resistance are used, or by making up the steel bars or collectors of a plurality of parts.

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The invention accordingly provides cathode systems for the electrolytic production of aluminum, which are divided in the direction of their long axis on the side of the power conduction from the cathode to the collector into at least two parts having a differing electrical resistances in such a way that the electrical resistance between the free ends of the collector to the part of the marginal zone of the cathode facing the collector is at least 1.2 times the electrical resistance between the free ends of the collector to the part of the middle of the cathode facing the collector. To achieve this, either the contact composition or the collector is divided into zones of differing resistance.

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For the present purposes, a cathode system is the combination of cathode block, the collector and the contact composition or ramming paste which effects the electrical contact between cathode block and collector.

One way of realizing the solution provided by the invention is to use different materials having a different contact resistance between the collector and the carbon material of the cathode along the length of the cathode systems. A further way is to use multipart collectors, with material and conduction cross section of the collector parts being chosen so as to give the desired resistance between a given point (facing the melt) of the cathode block and the free ends of the collectors.

The invention further provides processes for realising an electrical contact between cathodes and collectors by means of at least two contact compositions or ramming pastes having differing electrical conductivities, processes for producing suitable collectors having the multipart structure described and the use of different contact compositions or ramming pastes or multipart collector designs in cathode systems for the electrolytic production of metallic aluminum.

Detailed Description of the Preferred Embodiments

The contact or tamping composition serves to provide mechanical strength of the combination of collector and cathode and also to provide electrical contact between these parts of the cathode system. For example, it is customary to fill the gap between collector and cathode by pouring cast iron into it. An alternative is to use ramming pastes made up of particulate carbon (anthracite and/or graphite) and/or metal particles (powder, shoot, fibers, whiskers or platelets; in particular of iron or iron alloys such as steel) as filler and tars (in particular black coal tar) or pitches (in particular black coal pitch) as binder. The conductivity or

electrical resistance can be varied by choice of type (composition, particle size and particle size distribution) and amount of the conductive filler. It is likewise possible to use adhesives, in particular two-
5 component or multicomponent adhesives such as those based on epoxy resins or phenolic resins, which are likewise given the desired degree of conductivity by addition of particulate metal and/or carbon in the form of anthracite and/or graphite powders.

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Preference is given to using at least two different contact compositions or ramming pastes for establishing the contact between cathodes and collectors, with the boundary between zones of different materials running
15 perpendicular to the long axis of the collectors. The contact resistance between collector and cathode in the middle of the length of the cathode is lower than the contact resistance in the region of the ends of the cathode.

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Furthermore, it is preferred that the contact composition in the region of the middle of the cathode length is cast iron. The contact composition used in the region of the ends of the cathode length is preferably selected from
25 the group consisting of tars, tar pitches, synthetic resins based on epoxy resins and/or phenolic resins and adhesives based on epoxy resins and/or phenolic resins filled with electrically conductive particles.

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As electrically conductive particles, particular preference is given to particles comprising particulate carbon and metal particles in the form of powders, shoot, fibers, whiskers and/or platelets.

In "Light Metals 1999", edited by C.E. Eckert, Warrendale, PA, USA, Toda et al., describe studies on the contact resistance between collector rods and cathode material when using two different contact compositions of differing conductivity. Both the compositions studied led to a very low contact resistance of less than $0.1 \Omega/\text{mm}^2$. However, there is no suggestion of using contact compositions of differing conductivity side-by-side and thus setting a lower contact resistance in one zone than in an adjacent zone.

The division of the contact composition or the collector into zones of differing conductivity or differing electrical resistance is preferably carried out so that the current density at the contact interface between the cathode and the aluminum melt covering its surface is effectively uniform over the length of the cathode. For the purposes of the present invention "effectively uniform" refers to an embodiment in which the current density alters by no more than a factor of 2 over the length of the cathode. Preference is given to a change by a factor of not more than 1.5, particularly preferably by a factor of not more than 1.3.

If different contact compositions based on adhesives or contact compositions containing tars or pitches as binder are used, the recess on the underside of the cathode blocks is preferably filled with the contact compositions of differing resistance to such an extent that only small amounts exit upon installation of the collector rods. According to the invention, it is also possible to provide zones with electrical contact by casting molten metal, preferably cast iron, into the joins. The various possible ways of providing electrical contact can also be

realized in succession on the same cathode blocks.

The resistivity of the contact compositions chosen can easily be set in a targeted way by varying the components
5 of the composition. Here, the same binders or binder mixtures as matrix can be filled with different (in terms of type and/or amount) conductive additives; however, it is also possible to vary the binders or binder mixtures as a function of the type and amount of the conductive
10 filler in order to achieve a similar processing viscosity and thus even out the forces acting on the cathode block during installation.

Division of the collectors into zones having differing
15 resistances can be carried out so that the collector is divided into pieces of differing cross section, with the metals used being able to be identical or different, or into pieces composed of metals having differing conductivities, for example copper and steel. Of course,
20 it is also possible to vary cross section and material of the collector parts simultaneously. Owing to the fact that different metals usually have a different thermal expansion, preference is given to achieving the desired different resistance by use of the same metal and
25 different cross sections. However, it is also possible, according to the invention, to use different metals, and in this case metal parts having differing resistivities are then preferably arranged in the direction of the side of the carbon cathode facing the melt on a common support
30 made of a metal having a good conductivity (for example copper).

The zones of the collector having differing resistances are separated from one another by a sheet-like insulator.

Preference is given to using a mica sheet (because of its high thermal stability). The coherence of collectors assembled in this way is ensured by means of suitable fasteners, in particular sheet metal sleeves.

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Doing without such fasteners is also possible if a structure in which a metal bar made of a material having a good electrical conductivity is wrapped with an insulating film and a sheath made of material having a poorer conductivity. This sheathing is extended to such a distance that the bar is in direct contact with the carbon cathode in the middle of the cathode system length. In the outer region, i.e. toward the ends of the cathode system, electrical connection is effected exclusively via the sheath.

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In all cases, it is possible to use two collector half-rods or a single collector, where the single collector and the half-rods have been divided in a suitable manner into zones of differing resistance.

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Preferred embodiments of the invention are illustrated by the drawings. In these drawings,

25 fig. 1 shows a longitudinal section through a cathode system having two contact compositions of differing resistance; and

30 fig. 2 shows a cross section along the line II-II' through a cathode system having one collector which is connected to the cathode by means of a contact composition; and

fig. 3 shows a cross section along the line III-III'

through a cathode system having one collector which is connected to the cathode at this point by the join being filled with cast iron; and

- 5 fig. 4 shows a longitudinal section through a cathode end in which the collector (steel support) in two-part form can be seen; and
- 10 fig. 5 shows a longitudinal section through a cathode end in which the collector is made of different metals having differing conductivities; and
- 15 fig. 6 shows a longitudinal section through a cathode end in which the collector (steel support) in two-part form can be seen, and in which the configuration of the insulation with a right-angle fit is shown in an enlarged form; and
- 20 fig. 7 shows an alternative embodiment to that shown in fig. 6, here with an obtuse-angle fit; and
- 25 fig. 8 shows a longitudinal section through a cathode having a three-part collector; and
- 30 fig. 9 shows a cross section through a collector which is divided into two zones and whose parts are connected mechanically in an electrically insulating fashion by means of a sleeve; and
- 30 fig. 10 shows a cross section through the embodiment shown in fig. 4 along the line 'X-X'; and
- fig. 11 shows a cross section through the embodiment shown in fig. 4 along the line XI-XI'; and

fig. 12 shows a cross section through a collector which is divided into two zones and in which the zone having the higher resistance is configured in the form of a sheath.

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Fig. 1 shows a longitudinal section through a cathode system having a conventional collector rod 2 which is connected via two contact compositions 13 and 14 having different electrical resistances to the cathode 1. The contact resistance from the collector 2 through the contact composition 13 is greater than that via the contact composition 14, according to the invention by a factor of at least 1.2, preferably at least 1.5 and in particular a factor of at least 2. In a preferred embodiment, the material of the contact composition 14 is cast iron, while the material of the contact composition 13 is a tar pitch, synthetic resin or synthetic resin adhesive filled with carbon and/or metal particles.

Figs 2 and 3 show cross sections along the lines II-II' and III-III', respectively, through the cathode system of fig. 1. In these cases, too, the contact compositions 13 and 14 are chosen so that the contact resistance between the collector 2 and the cathode 1 at the positions of the sections II-II' (R^{II}) and III-III' (R^{III}) obeys the following relationship:
 $R^{III}:R^{II} = 1:1.2$ to $1:100$; preferably from $1:2$ to $1:80$ and in particular from $1:5$ to $1:60$.

Fig. 4 shows a longitudinal section through a cathode 1 with collector 2; the material 3 of the cathode is selected from the group consisting of graphite, semigraphitic carbon, semigraphitized carbon and amorphous carbon, with preference being given to graphite

cathodes because of their better conductivity. In this embodiment, the collector has two zones 4 and 5 which have differing electrical resistances because of their differing cross section. The materials 4 and 5 can be identical or different. The two zones 4 and 5 are electrically insulated from one another by an intermediate layer 6 of an insulating material which has to be able to withstand the operating temperature of the cathode of about 960 °C without damage. Preference is given to using mineral insulating materials such as mica sheets. The required mechanical strength is achieved in this embodiment by the zone 4 having the higher conductivity also having the larger cross section. In a further preferred embodiment, it is possible for the parts 5 and 4 of the collector to be joined to one another mechanically without being connected electrically.

This can be achieved, for example, by, as shown in fig. 9, a sleeve 15 made of a metal band, for example a steel band, being placed around the collector comprising the parts 4 and 5, with the sleeve 15 being insulated from the collector parts 4 and 5 by an insulator 6', for example an intermediate layer of mica. The parts 4 and 5 of the collector are electrically insulated from each other by an insulating intermediate layer 6. The clamp for the sleeve is not shown in this drawing.

Another embodiment of the invention with a multipart collector 2 is shown in fig. 5; here, the collector is composed of a thin plate 11 of a metal having a low resistance, for example copper, and two thicker plates 9 and 10 of a metal having a higher resistance but also a higher strength and stiffness, preferably steel. Plate 11

is electrically insulated from plate 9, but connected electrically to plate 10. As a result, the resistance of the path from the contact at the end 12 of the collector to the zone of contact between plate 10 and the cathode is lower than the resistance of the path from the contact at the end of the collector 12 to the zone of contact of plate 9 at the cathode 1. The specific electrical resistance of the materials of plates 9, 10 and 11 and their geometry (cross-sectional area) is chosen in accordance with what has been said supra so that the resistance from the end 12 of the collector to the zone of contact of the cathode 1 and plates 10 and 9 has a ratio of at least 1:1.2; in particular, the ratio of the resistances is selected so that the current density at the interface from the cathode 1 to the aluminum melt in the bottom of the cell is as uniform as possible. In this embodiment too, plates 9, 10 and 11 are mechanically joined to one another, as is illustrated in principle in fig. 9.

For the present purposes, "as uniform as possible" means that the ratio of the current density in the marginal zone to the current density in the middle zone of the cathode 1 is not more than 2:1, preferably not more than 1.5:1 and particularly preferably not more than 1.2:1.

Figs 6 and 7 show alternative embodiments of the insulation in the case of a two-part collector 2: in fig. 6, the collector part 4 has a recess bounded by a right angle, while in fig. 7 the recess in the part 4 has an obtuse angle. The embodiment shown in fig. 7 has been found to be advantageous for introducing the insulating intermediate layer 6. In a further preferred embodiment which is not shown, it is also possible to round the

angle so that a platelet-shaped mineral insulator such as mica does not break.

Fig. 8 shows a construction of a cathode system comprising a cathode 1 from which the electric current is conducted away via a collector 2. In this embodiment, the collectors 2 are each made up of three parts or zones 5, 7 and 8; once again, the sleeves are not shown for reasons of clarity.

The resistances in the embodiment with collectors having three zones of differing electrical resistance as shown in fig. 8 from the end 12 to zone 5 ($= R_{12/5}$), from the end 12 to zone 7 ($= R_{12/7}$) and from the end 12 to zone 8 ($= R_{12/8}$) preferably have the ratios shown in the following table:

Resistance ratio	$R_{12/5}:R_{12/8}$	$R_{12/5}:R_{12/7}$
Maximum	100	50
	Preferably 80	Preferably 45
	Particularly preferably 60	Particularly preferably 40
Minimum	1.5	1.2
	Preferably 2	Preferably 1.5
	Particularly preferably 30	Particularly preferably 10

When assembling collector and cathode block, it has to be ensured that in the region having a plurality of collector zones as in the embodiment shown in fig. 4 (longitudinal section) and fig. 9 (cross section) the electric current is conducted away only via the collector zone in contact with the cathode.

To achieve this, a sheet-like insulator, for example a mica sheet, is placed on the two sides of the collector corresponding to the length of the divided zones so that there is no electrical connection between the cathode and the zone of lower resistance of the collector in this region.

Fig. 10 shows a corresponding structure (section X-X' in fig. 4) in which insulating sheets 6'' and 6''' are placed on both sides of the collector in the region of the divided zones and can be fixed in position by means of the ramming paste 13. Otherwise, the ramming paste provides, in a known manner, electrical contact (here between the zone 5 and the cathode) and fixes collector 2 to cathode 1.

In the region of the section XI-XI' of the cathode system in fig. 4, which is depicted in fig. 11, such insulation at the side is naturally no longer necessary. For this reason, the contact resistance between the cathode 1 and the collector 2 via the ramming paste 13 is considerably lower in this region because of the larger contact area, which likewise leads to an increase in the current density in this region.

When the collectors are divided into more than two zones, insulation likewise has to be provided at the sides. The necessity for insulation at the sides can be avoided if the zone of higher resistance in the collector is configured not as a plate facing the cathode but rather in the form of a sheath which encloses the collector at least to an extent which allows contact via the ramming paste Fig. 12 shows a cross section of an embodiment of this type, with the inner part 4 of the collector 2 being

surrounded on three sides by a sheath 5 of higher resistance. Here, insulation 6 is necessary only in the interior of the collector; the lower cost of assembling the collector is balanced by the increased complexity of construction of this form, so that one or other form of this embodiment is preferred depending on the particular circumstances of the cell construction.

Examples:

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Example 1

Graphite cathodes of conventional construction having a length of 3 300 mm were provided with conventional steel supports as collectors and connected electrically by introduction of ramming pastes having differing resistances. Here, the ratio of the specific resistance of the tamping composition in the region near the edge to that in the central region is 5:1. An electrolysis cell equipped in this way with 20 cathode blocks was operated at a current of 220 kA and 4.4 V for 1 000 days. For comparison, cells were operated using the same cathode system but a uniform tamping composition.

25 After the period of operation indicated, the cells were emptied and dismantled, and the cathodes were examined for wear. While in the case of the cathodes having a uniform construction the removal of material in the two edge zones was about 7.5 cm and that in the middle of the cathode was only 2.5 cm, in the case of the configuration according to the invention the removal of material in the edge zones was measured as about 4 cm and that measured in the middle was about 3.5 cm.

Example 2

Graphite cathodes of conventional construction having a length of 3 300 mm were provided with conventional steel supports as collectors and connected electrically in a conventional way by introduction of a tamping composition. An electrolysis cell having 20 cathode blocks was operated at a current of 220 kA and 4.4 V for 1 000 days (comparison). According to the invention, the same cathodes were joined to steel supports like those shown as 2 in fig. 4 whose ends had been milled down to 5/6 of their original thickness to a distance of about 700 mm from the end of the cathode. The transition to the unmachined middle zone had an angle of about 160 ° as shown in fig. 7. The milled area was covered with a mica sheet 6 having a thickness of about 0.3 mm, and a steel plate 5 having appropriate dimensions was fastened on top of this at each end of the support with the aid of sleeves of the type shown in fig. 9 which were insulated with mica sheets.

The steel supports or collectors were insulated on both sides by insertion of mica sheets as in the construction shown in fig. 4 as far as the multipart zone of the collector extended, and joined to the cathode by means of a customary tamping composition.

After the period of operation indicated, the cells were emptied and dismantled, and the cathodes were examined for wear. While in the case of the cathodes having a uniform construction the removal of material in the two edge zones was about 8 cm and that in the middle of the cathode was only 2 cm, in the case of the configuration according to the invention the removal of material in the

edge zones was measured as about 3.5 cm and that measured in the middle was about 3 cm.

5 It was found that such cathode systems according to the invention make it possible to achieve a considerably more uniform corrosion of the cathodes with a significant reduction in the corrosion in the edge zone. Since the useful life of the cathode is limited by the region of greatest corrosion, use of cathode systems according to
10 the invention gives a significant increase in the life of the cathodes in a simple and relatively easy way.

List of reference numerals

1	Cathode
2	Collector
3	Material of the cathode (graphite, semigraphitic, semigraphitized or amorphous carbon)
4	Collector zone having a higher electrical conductivity than zone 5
5	Collector zone
6, 6', 6'', 6'''	Insulating intermediate layer
7, 8	Collector zones
9, 10	Metal plates having a high electrical resistance
11	Metal plates having a low electrical resistance
12	End of the collector
13	Tamping composition
14	Cast iron
15	Sleeve comprising a metal band